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APPLICATION FOR THE UNITED STATES PATENT

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Invention: SILICON SUBSTRATE COMPRISING POSITIVE ETCHING
PROFILES WITH A DEFINED SLOPE ANGLE, AND
PRODUCTION METHOD

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SILICON SUBSTRATE COMPRISING POSITIVE ETCHING PROFILES WITH A DEFINED SLOPE ANGLE, AND PRODUCTION METHOD

The invention relates to a silicon substrate with positive etching profiles with a defined slope angle. The invention concerns furthermore a method for the production of a silicon substrate with a positive etching profile with a defined slope angle.

The following can be generated with this method:

- silicon casting molds or silicon embossing tools for the production of polymer mold parts
- micro-fluid devices with channel systems and nozzles
- devices of power electronics with trench structures
- special bridge structures for devices of the electron microscopy or the like.

Numerous devices of the micro-system technology are produced on the basis of structured silicon substrates. This concerns in particular devices of the micro-mechanics, the micro-fluidic field and the power electronics. The process of silicon structuring is an important aspect in connection with the production of components.

The wet chemical etching of silicon substrates is described in the document J. P. John et al.: Journal electrochemical society, volume 140, No. 9 (1993), 2622 -- 2625. For example mixtures of nitric acid (HNO_3), fluoric acid (HF) and water can be employed for this purpose. The etching process runs completely iso-tropic in this case, that is the mask under etching is nearly as large as the etching depth. Limits for the application of this method result from the advancing minimization of the lateral structural dimensions, which minimization results from the requirement of increasing miniaturization of the device elements of the micro-system technology.

An aniso-tropic wet chemical structuring of silicon according to H. Seidel, L. Csepregi, A. Heuberger, H. Baumgaertel: Journal electrochemical society, volume 137, No. 11, Nov. 1990, 3612 -- 3632,4, respectively, B. Kim, D. D. Cho: Journal electrochemical society, volume 145, No. 7, July 1998, 2499 -- 2508 is possible by employment of an alkaline etching solution preferring directions, such as potassium hydroxide, lithium hydroxide, or sodium hydroxide. The non iso-tropic character of the etching is based on the different dissolution speeds of the silicon in the various crystal planes. The $\langle 111 \rangle$ - plane is most slowly abraded and therefore operates as a structural limitation. During etching of $\langle 100 \rangle$ -silicon thus there result frustrated pyramid like recesses where the (111) -faces form the structural walls with a defined

angle of 54.74 degrees. With a structural width b_M in the etching mask, there can be achieved a maximum etching depth A_t of

$$A_t = \frac{b_M}{\sqrt{2}}$$

Since the position of the crystal planes is fixed according to angle and grid, the realization possibilities for microstructures are substantially limited relative to lateral shape and cross-sectional shape of the etched trenches.

Various plasma supported silicon etching processes have been developed in connection with the quick development of semiconductor technology. A multitude of possible plant concepts for plasma etching plants and a multitude of process parameters enable the variation of the etching processes over a wide region. The plasma etching processes are associated in principle and in particular with the advantage, that an iso-tropic structuring is possible independent of the crystal orientation.

Plasma chemical silicon etch processes are based in most cases on the chemistry of fluorine. If silicon is etched for example in pure SF_6 plasma (SF_6 : sulfur hexa

fluoride), then the process runs usually iso-tropical, such that the mask under etching is approximately equal to the etching depth, compare H. von Boenig: Fundamentals of plasma chemistry and technology, p. 174, The research Institute of plasma chemistry and technology Carlsbad, California.

An anisotropy of the etching process can be obtained in the following way amongst others:

Employment of chlorine -bromine - fluorine chemistry

The lateral etching is prevented by passivation of the side wall. The composition of the etching gas is adjusted thus for this purpose that during the etching process also such chemical reactions occur, which reactions lead to the covering of the side walls with etch resistant layers, compare I. W. Ragelow, H. Loeschner: journal vacuum science and technology, B 13 (6), Nov./December 1995, 2394 -- 2399 and K.-M. Chang ,T.- H. Yeh, I. - C. Deng, H. - C. Lin: journal of applied physics -Sept. 1 1996, volume 80, issue 5, 3048 -- 3055.

The high expenditure for the safety technology as well as gas furnishing and gas discharge for assuring compatibility with the environment is a problem associated with this method.

Employment of fluorine chemistry in connection with oxygen

Frequently a mixture of SF_6 and oxygen is employed as an etching gas. The silicon reacts with the oxygen species to SiO_2 in the structures. The oxygen layer is quick to be again removed at the floor by fluorine radicals supported by ion impact as compared with the side walls, such that the etching process obtains a preferred direction. An optimum ratio between sufficient side wall passivation and high etching speed is very difficult to adjust. The control of the passivation limits the achievable etching depth, compare I. W. Rangelow, H. Loeschner: Journal vacuum science and technology, B 13 (6), Nov./December 1995, 2394 -- 2399 and others.

Employment of cryogenic processes in connection with SF_6 - O_2 chemistry

A high concentration of reactive etching species is the precondition to obtain high etching speeds. In this case however, a more intense etching attack occurs also on the side walls. The probability of spontaneous reactions between silicon and fluorine

at the side walls is reduced drastically by cooling of the substrates to temperatures of about -110 degrees centigrade. The lateral etching rate decreases together with the chemical reaction rate. However, an intensive ion impact occurs at the floor of the structures. This intensive ion impact generates radical places and excites reactive particles such that chemical reactions occur furthermore. A clearly increased vertical etching rate results therefrom, compare, compare I. W. Rangelow, H. Loeschner: Journal vacuum science and technology, B 13 (6), Nov./December 1995, 2394 -- 2399.

Advanced Silicon Etch Process' (ASE)

The ASE process is based on a known method according to the German printed Patent document DE 4241045 C1, which was developed by Laermer and Schilp. A cyclical process is here concerned, wherein the cyclical process is composed out of alternating deposition steps and etching steps. A passivation of the complete substrate surface occurs during the deposition interval by deposition of a polymer layer. During the etch interval, the polymer layer is removed on all horizontal planes by ion impact. The silicon laid bare reacts with fluorine to volatile reaction products at the floor of the structures.

Characteristic features of the ASE process include:

- realization of etching depth of from 10 to 500 micrometer
- achievable aspect ratio: larger than 25
- slope angle in the side walls: nearly 90 degrees
- mask under etching goes towards zero
- arbitrary lateral shape of the structures (for example channel structures, passage holes through the silicon wafer, comb like structures, grid structures)
- application of conventional etching masks (for example SiO_2 , photo resist)
- etching rate: three to five micrometers per minute

Based on the present state of the art it has to be determined that presently hardly any technological possibilities exist for varying the etching profile in the silicon structuring. These possibilities are limited essentially to the following two variations:

a) completely iso-tropic etching (for example by way of SF_6 - plasma)

A typical structure is illustrated in figure 1.

b) realization of silicon structures with completely vertical side walls with the mask underetchings nearly zero (compare figure 2).

Therefore the object of the Invention comprises to disclose a solution by way of which positive etching profiles with a defined slope angle β of the side walls can be generated.

According to the present Invention the object is achieved with the silicon substrate with the features stated in claim 1.

Furthermore the object is achieved by a method with the features recited in claim 2. According to the method the silicon substrate covered the mask is etched isotropically such that the mask under etching u is approximately equal to the etching depth A_t , in the following the etching depth is enlarged to such an extent that the mask under etching remains constant and the etching front obtains a new course, wherein the side walls of the structure are covered with a polymer in this step, whereupon the polymer is removed from the side walls of the structure. The previously recited steps are repeated as many times until the desired etching profile and the desired etching depth are generated.

Advantageous variations of the method result from the features recited in the subclaims.

The method according to the present Invention is a plasma etching process (PPE-process - positive profile etching process) which allows to structure silicon substrates such that thereby positive etching profiles are generated. The slope angle of the side walls of the etched structures can be defined adjusted in the region between 60 degrees and 88 degrees by suitable selection of the process parameters. Etching rates of three to five micrometers per minute and etching depth up to 200 μm can be obtained depending on the aspect ratio, on the opened (that is to be etched) face and on the process variation. A limitation of the reachable etching depth results only from the standing time of the etching masks, however not from process associated parameters.

The Invention is in the following illustrated in more detail by way of embodiment examples. There is shown in the drawings:

Figure 1 a typical structure according to an iso-tropic etching process in pure SF_6 plasma

Figure 2 a structure generated by the ASE - process

Figure 3 a desired etching profile with defined slope angle β

Figure 4 a schematic construction of a plasma etching plant

Figure 5 a silicon wafer with an etching mask

Figure 6 a result of the iso-tropic silicon etching in pure SF_6 plasma

Figure 7 a result after iso-tropic silicon etching and followed by a modified ASE process

Figure 8 a laying bare of the side walls of the edge structure with a O_2 - plasma

Figure 9 a presentation of the dependence of the slope angle of the edge structure from the time ratio Z

Figure 10 a structure with a slope angle $\beta = 89$ degrees, etched at $Z = 0.1$

Figure 11 a structure with a slope angle $\beta = 85$ degrees, etched at $Z = 0.167$

Figure 12 a structure with a slope angle $\beta = 83$ degrees, etched at $Z = 0.25$

Figure 13 a structure with a slope angle $\beta = 81$ degrees, etched at $Z = 0.33$

Figure 14 a structure with a slope angle $\beta = 77$ degrees, etched at $Z = 0.5$

Figure 15 a structure with a slope angle $\beta = 74$ degrees, etched at $Z = 0.67$

Figure 16 a structure with a slope angle $\beta = 66$ degrees, etched at $Z = 1$

Figure 17 a structure with a slope angle $\beta = 60$ degrees, etched at $Z = 2$

Figure 18 an embossing tool out of silicon

Figure 19 two structures made in silicon with a Y-shaped etching profile

Figure 20 a silicon structure for liquid storage cells

Figure 21 a trench in silicon with slightly inclined side walls

Figure 22 a metal bridge structure on silicon

Figure 23 a Cu - bridge structure, produced by way of the PPE -process

Figure 24 a Cu - bridge laid bare

The figures 1 and 2 serve for illustrating the state-of-the-art. Figure 1 shows a typical structure according to an iso-tropic etching process in a pure SF_6 - plasma. Figure 2 shows a structure generated by the ASE - process. Figure 3 shows schematically the desired positive etched profile with the illustrated slope angle β .

A plasma etching plant of the company Surface Technology Systems Ltd. (STS), Great Britain is suitable for performing the structuring of the silicon substrate according to the present Invention as illustrated in figure 3. Such a plant is the schematically illustrated in figure 4.

4" or 6" silicon wafers can be processed in this plant. The plasma reactor is fed through a sluice 1. The silicon wafers are held by a mechanical clamping 3 on the

substrate electrode and are cooled by way of helium backside cooling. A pump system comprising a rotary slider pump 4 and a turbo molecular pump 5 is furnished for vacuum generation. The gas pressure of the process can be set in the range of 1 to 15 Pa. Nitrogen (N_2), oxygen (O_2), argon (Ar), tetra fluoro methane (CF_4), sulfur hexa fluoride (SF_6) and octa fluoro cyclo butane (C_4F_8) can be fed in as process gases through a gas inlet port 7. A main component of the plant is the highly sealed ICP - plasma source 6, wherein a high frequency power of maximum one kilo Watt can be coupled into the ICP - plasma source 6. The substrate electrode is capable of being biased and can be charged with a high frequency power of maximum 300 watts. An adapter network 8 and a high frequency generator 9 are furnished for this purpose. In each case the frequency amounts to 13.56 MHz. The performance of cyclical processes is possible at the plant.

The measurement of etching depth can be performed with the aid of a surface profile meter of the company TENCOR INSTRUMENTS with an accuracy of plus minus 5 nm.

The method according to the present Invention, the so-called PPE - process is performed cyclically. The method is composed out of three steps, wherein the three

steps are repeated always in the same sequence. The method exhibits the following course.

It is noted that the silicon substrate is furnished with an etching mask as shown in figure 5. Here mask materials such as photo resist, thermal silicon oxide (SiO_2), photo resist and SiO_2 combined as well as metal masks of aluminum or copper are employed.

According to a first step the silicon substrate is iso-tropically etched in a pure SF_6 - plasma according to the representation shown in figure 6. With this etching step the mask under etching u is approximately equal to the etching depth A_t .

According to a second step the silicon substrate is subjected to a modified ASE - process as shown in figure 7. Since the ASE - process etches absolutely vertically, thereby the etching depth is increased but the mask under etching remains constant, and the etching front obtains a new course. The side walls of the structures are covered with a polymer according to the ASE - process.

According to a third step the polymer at the side walls of the structure is removed by O_2 -RIE and an etched structure is obtained as shown in figure 8.

The method steps 1 to 3 are now repeated so many times until the desired etching depth has been reached. By superposition of the etching fonts, which result from the two silicon etching processes according to the steps a) and b), there are generated positive etching profiles with a slope angle between 60 degrees and 88 degrees.

The process parameters for each interval are contained in table 1. The parameters of the modified ASE - process are disposed opposite to those of the known Bosch process in table 2. A reproducible setting of a desired slope angle is possible by the selection of suitable time ratio Z for the steps 1 and 2.

$$Z = \frac{t_{\text{SF}_6\text{-RIE}}}{t_{\text{ASE(modified)}}}$$

The larger the time part of the iso-tropic etching in pure SF_6 - plasma, the smaller the slope angle becomes. Figure 9 shows this relationship. The figures 10 to 17 show examples for real structures with the decreasing slope angle β , which were correspondingly etched.

Embodiment 1

Structured silicon substrates can be employed as molds for the casting of devices of polymers or other substances capable of being cast. The result of the silicon structuring is of decisive importance for the capabilities of separating the cast parts from the mold. The slope angles of the side walls smaller than 90 degrees alleviate the removal of the formed parts substantially. Figure 18 shows a silicon structure with a slope angle of 88 degrees, where the silicon structure is suitable as an embossing tool for the production of polymer parts with channel structures for medical technology.

Embodiment 2

Micro-fluidic devices contain frequently channel systems and nozzles, where the channel systems and nozzles are generated by corresponding structuring of silicon substrates. Increasingly the requirement exists in this context to realize structures with complex lateral forms and vertical forms. This contains amongst others the generation of structures with composed etching profile all of etching profiles with alternating slope angle. Examples for this are shown in figures 19 a) and b).

Embodiment 3

Storage cells for liquids can for example have a shape as is shown in figure 20. The illustrated structures have also been generated by the method according to the present Invention.

Embodiment 4

Frequently the trenches are etched into silicon in the context of the production of devices of the power electronics, wherein the trenches are in the following covered with dielectrics or, respectively, are filled with metals. Capacitors or through contacts are to be generated in this manner. The homogeneous coating and void free filling of the trenches is alleviated, if the slope angle is disposed between 85 and 88 degrees. Figure 21 shows an example for such a trench.

Embodiment 5

Special metal bridge structures on silicon are required in the field of electron microscopy. A free metal bridge, which is connected to contact pads can be generated on the silicon substrate for such a case (figure 22).

The laying bare of such metal bridges represents up to now a problem for the silicon structuring. On the one hand the silicon on the backside of the metal strip is to be completely removed up to an etching depth of from 200 up to 500 micrometers, and on the other hand a minimum under etching of the SiO_2 under the contact pads is desired. Despite miniaturization of the device element, the stability of the structure should therewith remain assured. The figures 23 and 24 show structures of this kind realizable with the Invention method.

List of reference numerals

- 1 - sluice
- 2 - silicon wafer
- 3 -mechanical clamping
- 4 - rotary slider pump
- 5 - turbo molecular pump
- 6 - ICP - plasma source
- 7 - gas inlet port
- 8 - adapter network
- 9 - high frequency generator